Large magnetic entropy change and refrigerant capacity in rare-earth intermetallic RCuAl (R=Ho and Er) compounds

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A R T I C L E   I N F O

Article history:
Received 27 August 2011
Received in revised form
14 March 2012
Available online 1 April 2012

Keywords:
ZnNiAl type
Magnetic entropy change

A B S T R A C T

The magnetic properties and the magnetocaloric effects of RCuAl (R=Ho and Er) compounds have been investigated. Both HoCuAl and ErCuAl just undergo a second-order ferromagnetic–paramagnetic phase transition at Tc. Large reversible magnetic entropy changes (ΔSM) are observed around their respective Curie temperatures due to the ferromagnetic–paramagnetic phase transition. For a field change of 0–5 T, the peak values of −ΔSM of RCuAl (R=Ho and Er) compounds are 23.9 and 22.9 J kg⁻¹ K⁻¹ at Tc, with the values of refrigerant capacity of 393 and 321 J kg⁻¹, respectively. These properties suggest that RCuAl (R=Ho and Er) compounds could be considered as attractive magnetic refrigerants working in low temperature range.

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Recently, much attention has been paid to magnetic refrigeration based on the magnetocaloric effect (MCE) of solid-state working substances [1–4]. Magnetocaloric materials with a first-order phase transition have been widely investigated due to their large isothermal magnetic entropy change (ΔSm), an important parameter for evaluating the magnitude of MCE. However, some problems such as hysteresis and time dependence, which exist almost universally in magnetocaloric materials with a first-order phase transition, should be solved before this kind of materials is practically used. Magnetocaloric materials with a second-order phase transition may have a lower peak value of ΔSm, whereas this could be compensated by their large refrigerant capacity (RC), which is a more crucial parameter for evaluating the technological significance in a refrigerant material. Therefore, it is necessary to explore new magnetocaloric materials with a second-order phase transition.

RCuAl (R=heavy rare-earth) compounds each crystallizing in a hexagonal ZnNiAl-type structure belong to a large family of terminal RTX (T=transitional metal, X=p-metal) intermetallics. All the R atoms and Al atoms occupy 3g and 3f sites, respectively. Cu atoms occupy two non-equivalent 1b and 2c positions [5]. Two types of basal plane layers are alternately distributed along the c-axis: one contains all the R atoms and one-third of Cu atoms, and the other comprises a nonmagnetic layer formed by all the Al atoms and two-thirds of Cu atoms (see the inset of Fig. 1). The distinct layered character of the crystalline structure may lead to large magnetocrystalline anisotropy.

In the recent years, magnetic structures, phase transitions, and magnetic properties for RCuAl (R=Gd–Er) compounds have been investigated in detail by neutron diffraction, specific heat, and magnetic measurements [6–11]. Uniaxial magnetic anisotropies in GdCuAl, DyCuAl and ErCuAl and a basal-plane type of magnetic anisotropy in HoCuAl have been found. The magnetic structure is collinear whereas the spins are not parallel to the c-axis for TbCuAl. In previous work, we have reported the magnetic properties and magnetocaloric effects of RCuAl (R=Gd, Tb and Dy) compounds [12–14]. Large reversible magnetocaloric effects make them attractive candidates for magnetic refrigeration. In this paper, MCEs and refrigerant capacities of RCuAl (R=Ho and Er) compounds with diverse magnetic anisotropy are reported contrastively. Large ΔSm and RC are obtained for RCuAl (R=Ho and Er) compounds around their respective Curie temperature. For a field change of 0–5 T, the maximum values of −ΔSm are 23.9 and 22.9 J kg⁻¹ K⁻¹ for RCuAl (R=Ho and Er) compounds, respectively. The corresponding RC values reach 393 and 321 J kg⁻¹ for the same field change.

The RCuAl (R=Ho and Er) ingots were prepared by arc melting Al, with a purity of 99.99 wt%, and R and Cu, with a purity of 99.9 wt%, in a high-purity argon atmosphere. 5 at% excess Ho and 2 at% Er were used to compensate the weight loss during the arc melting. The melt-spun ribbons were obtained by using a single-roller melt-spinner at a cooper wheel surface speed of 50 m/s. A post-annealing of the products at 873 K for 100 h and
compounds. The nonexistence of Cu or the reaction between Al and the residual Oxygen in the furnace may during the arc melting leads to the excess of Cu and Al. The Er during the arc melting indicates that HoCuAl also experiences only a ferromagnetic-paramagnetic phase transition and shows a basal-plane type magnetic anisotropy. The impure phase Al₂O₃ does not affect obviously the shape of thermal magnetization curves due to its diamagnetism. Therefore, the discrepancy between ZFC and FC M–T curves for R CuAl (R=Ho and Er) compounds may be attributed to the domain wall pinning effect.

The nature of magnetic phase transition and MCEs of R CuAl (R=Ho and Er) compounds are investigated via the measurements of isothermal magnetization curves at different temperatures. The Arrott plots [15] and the temperature dependences of ΔM₉₅ for R CuAl (R=Ho and Er) compounds are displayed in Fig. 3. The positive slopes of Arrott plots near Tₘ confirm the second-order FM–PM transition, which accords well with the case mentioned based on Fig. 2 where thermal hysteresis around Tₘ is absent. From the right panels of Fig. 3, one can find that both HoCuAl and ErCuAl compounds exhibit large ΔM₉₅ around their respective Curie temperatures. For a magnetic field change of 0–2 T, the peak value of –ΔM₉₅ for R CuAl (R=Ho and Er) compounds are 14.0 and 14.7 J kg⁻¹ K⁻¹, respectively.

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Besides the peak value of ΔM₉₅, RC is another important parameter for characterizing the MCE. In the present paper, the value of RC is calculated by numerically integrating the area under the ΔM–T curve, with the temperatures at half maximum of the peak taken as the integration limits [22]. Large RC values of 393 J kg⁻¹ and 321 J kg⁻¹ are obtained in R CuAl compounds with R=Ho and Er for a magnetic field change of 0–5 T, respectively. The RC of HoCuSi is also calculated from the –ΔM₉₅ versus T curve in Ref. [21] by the same method. The evaluated value of RC for HoCuSi is 385 J kg⁻¹ for the same field change, which is slightly less than that of HoCuAl, although the ΔM₉₅ value of the former is much larger than that of the latter. Moreover, the RC of HoCuAl is also comparable to that of ErAl₃ (RC=397 J kg⁻¹ for a field change of 0–5 T), though the ΔM₉₅ value for ErAl₃ reaches 40 J kg⁻¹ K⁻¹ at Tₘ=13 K [23].

In conclusion, the R CuAl (R=Ho and Er) compounds with the hexagonal ZrNiAl-type structure show large reversible ΔM₉₅ around their respective Curie temperatures. For a magnetic field

Fig. 1. X-ray diffraction patterns of R CuAl (R=Ho and Er) compounds at room temperature. Inset: schematic drawing of the ZrNiAl-type unit cell of R CuAl.

Fig. 2. ZFC (open symbol) and FC (closed symbol) temperature-dependent magnetizations under a magnetic field of 0.05 T for R CuAl (R=Ho and Er) compounds.
change of 0–5 T, the maximum values of $-\Delta S_m$ for $RCuAl (R=Ho$ and Er) compounds are 23.9 and 22.9 J kg$^{-1}$ K$^{-1}$, respectively. Corresponding large RC values are also obtained, which are 393 and 321 J kg$^{-1}$ K$^{-1}$ for the same field change. The large $\Delta S_m$ and the high RC as well as no hysteresis loss make $RCuAl (R=Ho$ and Er) compounds promising candidates for magnetic refrigeration near liquid-helium temperatures.

This work is supported by the National Natural Science Foundation of China (Grant nos. 50731007, 11004204 and 51001077), the Hi-Tech Research and Development Program of China, the Knowledge Innovation Project of the Chinese Academy of Sciences, and the opening project of the Key Laboratory of Cryogenics, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences.

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